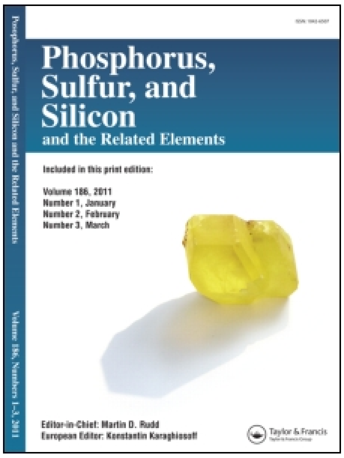

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STUDIES ON THE STABILITIES OF ALKYLMETHYLAMMONIUM SALTS OF MONOMETHYL ESTERS OF PHOSPHONIC ACIDS

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STUDIES ON THE STABILITIES OF ALKYLMETHYLAMMONIUM SALTS OF MONOMETHYL ESTERS OF PHOSPHONIC ACIDS

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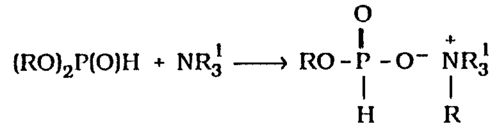
It has been shown by ^{1}H NMR spectroscopy that alkylmethylammonium salts of monomethyl esters of phosphonic acids having the general formula $[R\overset{+}{N}H_2CH_3][^-OPH(O)(OCH_3)]$ are unstable. At ambient temperature these salts convert into the corresponding alkylammonium salts $[R\overset{+}{N}H_3][^-OPH(O)(OCH_3)]$. The effect of different substituents R on the stability of these alkylammonium cations is discussed.

Key words: Dimethyl phosphonate; amines; alkylation.

INTRODUCTION

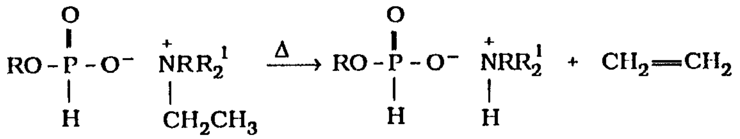
Dialkyl phosphonates react with amines[1–6] to yield the corresponding alkylammonium salts of the monomethyl ester of the phosphonic acid **1** (Equation (1)).



$$(RO)_2P(O)H + NR^1_3 \longrightarrow RO-\underset{H}{\overset{O}{\overset{\|}{P}}}-O^- \ \underset{R}{\overset{+}{N}}R^1_3 \qquad (1)$$

1

These alkylammonium salts **1** that have at least one ethyl group in the cation, undergo the Hoffman elimination of ethylene at elevated temperatures[7] (Equation (2)). By



$$RO-\underset{H}{\overset{O}{\overset{\|}{P}}}-O^- \ \underset{CH_2CH_3}{\overset{+}{N}}RR^1_2 \xrightarrow{\Delta} RO-\underset{H}{\overset{O}{\overset{\|}{P}}}-O^- \ \underset{H}{\overset{+}{N}}RR^1_2 + CH_2{=}CH_2 \qquad (2)$$

contrast, it has been established[8,9] that alkylammonium salts of monomethyl esters of phosphonic acids are unstable at room temperature. This instability is manifested by a decrease in the integrated intensity of the NCH_3 protons as the reaction shown in Equation (1) progresses.

This present paper, which represents a continuation of our investigations on the interaction of dialkyl phosphonates with amines,[5–10] is focused on investigating the effect of different functional groups on the stability of these alkylammonium salts of monomethyl esters of phosphonic acids.

EXPERIMENTAL

Dimethyl phosphonate, propylamine, ethylenediamine, *N,N*-dimethylaniline and triethylamine (Fluka) were distilled prior to use. ^1H NMR spectra were obtained on a GE Omega 400 NMR spectrometer using solutions in $CDCl_3$. Reactions were stirred using a Teflon coated stir bar and a magnetic stirrer.

1. Interaction of Dimethyl Phosphonate with Propylamine. Dimethyl phosphonate 3.6 g (0.033 moles) and propylamine 2.2 g (0.036 moles) were mixed in a round bottomed flask at 5°C. The mixture was stirred for 24 hrs at 5°C. The yield of methylpropylammonium salt of monomethyl ester of phosphonic acid as determined by ^1H NMR spectroscopy is quantitative.

1.1 Stirring of the methylpropylammonium salt of monomethyl ester of phosphonic acid at room temperature. The methylpropylammonium salt of the monomethyl ester of phosphonic acid 5.07 g (0.03 moles) was stirred for 15 hours at room temperature. The ^1H NMR spectrum of the reaction products was obtained and the data are given in Table I.

1.2 Stirring of the methylpropylammonium salt of monomethyl ester of phosphonic acid at 50°C and vacuum. The methylpropylammonium salt of the monomethyl ester of phosphonic acid 3.4 g (0.02 moles) was stirred for 24 hrs at 50°C and vacuum 0.1 mm Hg. The yield of the propylammonium salt of the monomethyl ester of phosphonic acid is quantitative as determined by ^1H NMR spectroscopy. The data are collected in Table I.

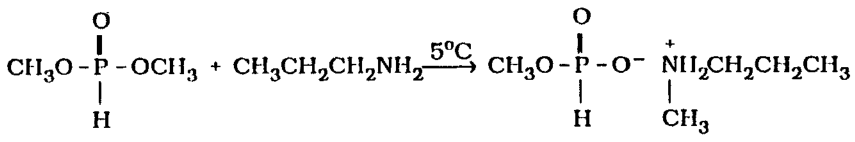
2. Interaction of dimethyl phosphonate with ethylenediamine. Dimethyl phosphonate 5.5 g (0.05 moles) dissolved in 5 ml methanol was mixed with 12.0 g (0.2 moles) ethylenediamine dissolved in 15 ml methanol at 20°C. The mixture was stirred for 2 hrs at 50°C. The methanol is removed by distillation at room temperature under reduced pressure, followed by removal of excess of ethylenediamine by distillation at a temperature not exceeding 50°C and a pressure of 0.2 mm Hg. The yield of ethylenediamine-ammonium salt of monomethyl ester of phosphonic acid is quantitative as determined by ^1H NMR spectroscopy. The data are collected in Table I.

3. Interaction of dimethyl phosphonate with N,N-dimethylaniline. Dimethyl phosphonate 5.5 g (0.05 moles) and 6.1 g (0.05 moles) *N,N*-dimethylaniline were mixed at room temperature. The mixture was stirred for 4 hours at 130°C. The reaction product was isolated by crystallization in absolute ethanol. The yield of the trimethylanilineammonium salt of the monomethyl ester of phosphonic acid is 10.6 g (92%).

4. Interaction of dimethyl phosphonate with triethylamine. Dimethyl phosphonate 5.5 g (0.05 moles) and triethylamine 5.05 g (0.05 moles) were mixed at room temperature. The mixture was stirred for 6 hours at 70°C. The yield of the methyltriethylammonium salt of the monomethyl ester of phosphonic acid is quantitative as determined by ^1H NMR spectroscopy. The data are collected in Table I.

RESULTS AND DISCUSSION

The reaction of dimethyl phosphonate with propylamine at 5°C gives the corresponding methylpropylammonium salt of the monomethyl ester of phosphonic acid **2** (Equation (3)). The ^1H NMR spectrum, in addition to resonances for the propyl group,

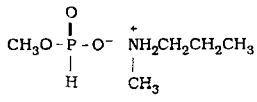
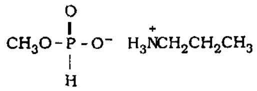
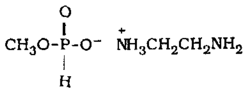
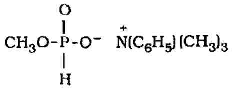
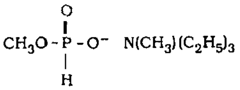


$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_3 + CH_3CH_2CH_2NH_2 \xrightarrow{5^oC} CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^- \underset{\underset{CH_3}{|}}{\overset{+}{N}}H_2CH_2CH_2CH_3 \quad (3)$$

2

TABLE I

Data from ${}^1H$ NMR spectra of the products obtained in the interaction of dimethylphosphonate with: propylamine; ethylenediamine, *N*-*N*-dimethylaniline and triethylamine

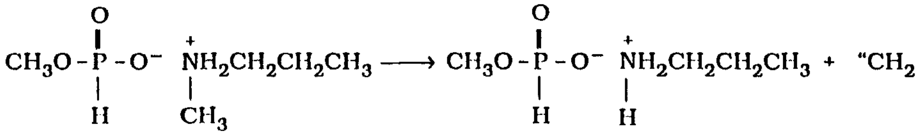
Compound	${}^1H$ NMR, δ [ppm]	Reaction Conditions Temp. °C	Time, hrs.	Vacuum mm Hg	Proton Integration Ration $POCH_3 : \overset{+}{N}CH_3$
1	**2**	**3**	**4**	**5**	**6**
 $CH_3O\text{-}\overset{O}{\underset{H}{P}}\text{-}O^-\ \underset{CH_3}{\overset{+}{N}}H_2CH_2CH_2CH_3$ **2**	0.86 (t, ${}^3J(HH)$ = 7.7 Hz, 3H) 1.57-173 (m, ${}^3J(HH)$ = 7.7 Hz, 2H) 2.66 (t, ${}^3J(HH)$ = 7.7 Hz, 2H) 3.21 (s, 3H) 3.40 (d, ${}^3J(PH)$ = 11.9 Hz, 3H) 6.61 (d, ${}^1J(PH)$ = 607.4 Hz, 1H) 8.56 (broad s, 2H)	5	24	-	1 : 1
Mixture of **2** and **3**	Except for the above mentioned signals there is a new signal at δ = 2.2 ppm, (s).	20	15	-	1 : 0.66
 $CH_3O\text{-}\overset{O}{\underset{H}{P}}\text{-}O^-\ H_3\overset{+}{N}CH_2CH_2CH_3$ **3**	0.86 (t, ${}^3J(HH)$ = 7.7 Hz, 3H) 1.57-1.73 (m, ${}^3J(HH)$ = 7.7 Hz, 2H) 2.66 (t, ${}^3J(HH)$ = 7.7 Hz, 2H) 3.40 (d, ${}^3J(PH)$ = 11.9 Hz, 3H) 6.61 (d, ${}^1J(PH)$ = 607.4 Hz, 1H) 8.56 (broad s, 3H)	50	24	0.1	There is no signal for NCH_3 protons
 $CH_3O\text{-}\overset{O}{\underset{H}{P}}\text{-}O^-\ \overset{+}{N}H_3CH_2CH_2NH_2$ **4**	2.60 (s, 2H) 2.78 (s, 2H) 3.31 (d, ${}^3J(PH)$ = 11.8 Hz, 3H) 6.03 broad singlet 6.49 (d, ${}^1J(PH)$ = 587.4 Hz, 3H)	50	2	0.2[a]	There is no signal for NCH_3 protons
 $CH_3O\text{-}\overset{O}{\underset{H}{P}}\text{-}O^-\ \overset{+}{N}(C_6H_5)(CH_3)_3$ **6**	3.51 (d, ${}^3J(PH)$ = 12.0 Hz, 3H) 3.91 (s, 9H) 6.86 (d, ${}^1J(PH)$ = 604.0 Hz, 1H) 7.42-8.21 (m, 5H)	130	4	-	1 : 9
 $CH_3O\text{-}\overset{O}{\underset{H}{P}}\text{-}O^-\ N(CH_3)(C_2H_5)_3$ **7**	1.05 (t, ${}^3J(HH)$ = 7.07 Hz, 9H) 2.92 (s, 3H) 3.29 (q, ${}^2J(HH)$ = 7.2 Hz, 6H) 3.51 (d, ${}^3J(PH)$ = 12.0 Hz, 3H) 6.60 (d, ${}^4J(PH)$ = 603.8 Hz, 1H)	70	6	-	1 : 1

[a] Vacuum was used when the excess of ethylenediamine was removed

shows a singlet resonance at δ 3.21 for the NCH_3 group, and a doublet at δ 3.40 for the $POCH_3$ group. The integrated intensity ratio between the $POCH_3$ and NH_3 protons is 1:1. The ${}^{31}P$ NMR spectrum of **2** shows a doublet of quartets at δ 7.38 with ${}^1J(PH)$ = 598.3 Hz and ${}^3J(PH)$ = 11.8 Hz. These NMR spectral data confirm the structure of the product **2**.

Continued stirring of this product **2** at room temperature leads to changes in the ^1H NMR spectrum of the reaction mixture. In addition to the resonances that are still present for **2**, a new singlet resonance begins to appear at δ 2.20. After 15 hours the integrated intensity ratio between the $POCH_3$ and NCH_3 protons is now 1:0.66. This change in the integral intensity ratio is due to a decrease in the intensity of the $\overset{+}{N}CH_3$ protons. At the same time, a corresponding increase of the integral intensity of the $\overset{+}{N}H_2$ protons is observed. It has been established that a volatile product separates during the stirring of **2** at room temperature. The ^1H NMR spectrum of this volatile product shows a singlet resonance at δ 2.20.

In order to accelerate this secondary reaction we have carried it out at 50°C rather than at room temperature. This experiment reveals that during stirring at 50°C under vacuum the product **2** converts into the propylammonium salt of the monomethyl ester of phosphonic acid **3**, along with a volatile product (Equation (4)). The ^1H NMR spectrum

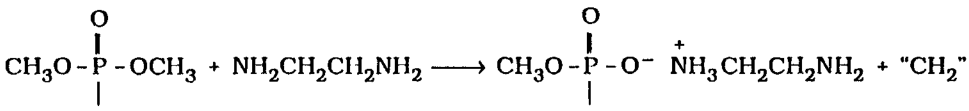


$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^- \ \underset{\underset{CH_3}{|}}{\overset{+}{N}}H_2CH_2CH_2CH_3 \longrightarrow CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^- \ \underset{\underset{H}{|}}{\overset{+}{N}}H_2CH_2CH_2CH_3 + \text{"}CH_2\text{"} \qquad (4)$$

2 **3**

of the product **3**, in addition to resonances for the propyl group, shows resonances due to the $POCH_3$, PH and NH groups at δ 3.40 (d, 3H, $^3J(PH)$ = 11.9 Hz), δ 6.61 (d, 1H, $^1J(PH)$ = 607.4 Hz) and δ 8.56 (br, s, 3H). In the ^1H NMR spectrum of **3** there is no singlet at δ 3.21 ppm which is characteristic of an NCH_3 group. In addition, there is not a resonance at δ 2.2 for the volatile product formed along with **3** because it has been removed under the low pressure conditions of the reaction. The ^{31}P NMR spectrum of **3** shows a doublet of quartets due to the PH group at δ 5.55 with $^1J(PH)$ = 614.9 Hz and $^3J(PH)$ = 12.0 Hz. The ^{13}C NMR spectrum of **3** shows a quartet for the CH_3 carbon at δ 9.67, with $^1J(CH)$ = 128.0 Hz. In addition there is a triplet for the CH_2 carbon atom δ 19.3, with $^1J(CH)$ with 124.2 Hz, a triplet for the NCH_2 carbon at δ 39.44, with $^1J(CH)$ = 142.0 Hz, and a quartet for the $POCH_3$ carbon at δ 48.9 Hz, with $^1J(CH)$ = 142.0 Hz.

The ^1H NMR spectrum of the product obtained from the reaction of dimethyl phosphonate with an excess of ethylenediamine shows it to be the ethylenediamineammonium salt of monomethyl ester of phosphonic acid **4** (Equation (5)). The singlet resonance in the spectrum at δ 2.78 can be assigned to the $\overset{+}{N}CH_2$

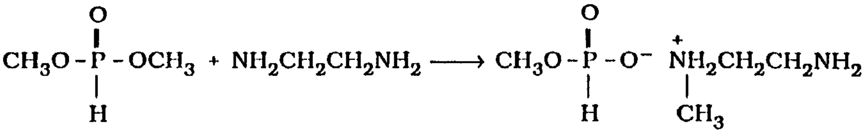


$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_3 + NH_2CH_2CH_2NH_2 \longrightarrow CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^- \ \overset{+}{N}H_3CH_2CH_2NH_2 + \text{"}CH_2\text{"} \qquad (5)$$

4

protons, with the resonance for the NCH_2 protons appearing at δ 2.60. This shift of the resonance to low field for the $\overset{+}{N}CH_2$ group is due to the presence of the positive charge on the nitrogen atom.

The ^{31}P NMR spectrum of **4** shows a doublet of quartets resonance at δ 9.13 with $^1J(PH) = 634.8$ Hz and $^3J(PH) = 11.5$ Hz. The ^{13}C NMR spectrum of **4** shows a singlet resonance due to the CH_2N carbons at δ 41.46, and a doublet resonance due to the $POCH_3$ carbon at δ 53.30 with $^2J(PC) = 3.1$ Hz. Apparently the first step of the reaction involves alkylation of ethylenediamine by diethyl phosphonate, and formation of the mono methylammonium salt of ethylenediamine **5** is formed (Equation (6)). Under the reaction conditions, **5** converts into **4** in the second stage of the reaction, a conversion that is



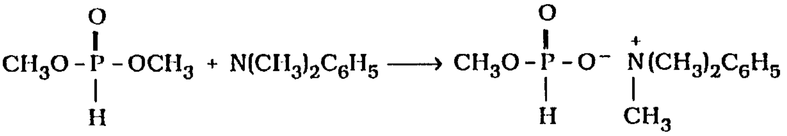
$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_3 + NH_2CH_2CH_2NH_2 \longrightarrow CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^-\ \underset{\underset{CH_3}{|}}{\overset{+}{N}}H_2CH_2CH_2NH_2 \qquad (6)$$

5

accompanied by the evolution of a volatile compound.

In reactions **4** and **5** we observe the formation of a volatile compound that we identify by the formula "CH_2". This compound has not yet been unambiguously identified, but it apparently has a characteristic singlet in the ^1H NMR spectrum at δ 2.20.

We have also studied the interaction at 130°C between dimethyl phosphonate and *N*,*N*-dimethylaniline, a tertiary amine having an aromatic substituent. The ^1H NMR spectrum of the product shows that the intensity ratio of the $POCH_3$ and $N(CH_3)_3$ protons

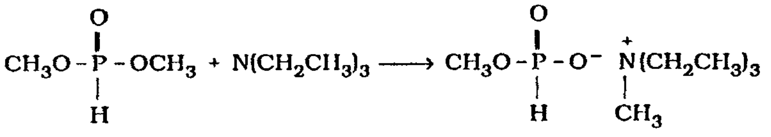


$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_3 + N(CH_3)_2C_6H_5 \longrightarrow CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^-\ \underset{\underset{CH_3}{|}}{\overset{+}{N}}(CH_3)_2C_6H_5 \qquad (7)$$

6

is 1:9, which indicates that the product **6** is stable at 130°C. The ^{31}P NMR spectrum of the product **6** shows a doublet of quartets resonance for the $POCH_3$ group at δ 3.45 with $^1J(PH) = 632$ Hz and $^3J(PH) = 11.8$ Hz. These data confirm that the structure of the product **6** is that shown in Equation (7).

The interaction between dimethyl phosphonate and triethylamine, a fully alkylated tertiary amine, has been studied at 70°C. This reaction is shown in Equation (8). The ^1H



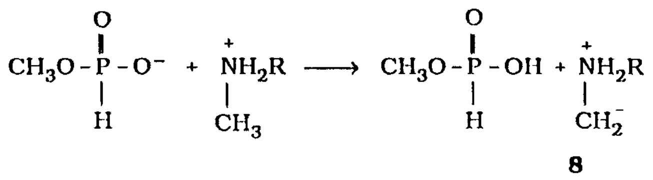
$$CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_3 + N(CH_2CH_3)_3 \longrightarrow CH_3O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O^-\ \underset{\underset{CH_3}{|}}{\overset{+}{N}}(CH_2CH_3)_3 \qquad (8)$$

7

NMR spectral data again confirm that the reaction product **7** is the methyltriethylammonium salt of the monomethyl ester of phosphonic acid. The ^{31}P NMR spectrum of **7** shows a doublet of quartets resonance at δ 3.38 with $^1J(PH) = 548.3$

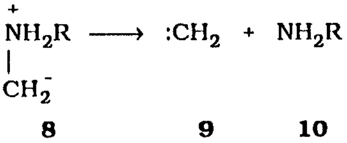
Hz and $^3J(PH) = 12.0$ Hz. The intensity ratio between the $POCH_3$ and NCH_3 protons is 1:1, which indicates that **7** is stable at a temperature of 70°C.

These results show that quaternary ammonium salts of the monomethyl ester of phosphonic acid are stable at temperature up to 70°C or 130°C, while alkylammonium salts of the monomethyl ester of phosphonic acid are unstable at room temperature. The difference in the stability of the salts is obviously due to the type of substitutent on the nitrogen atom. In the case of the alkylammonium salts, the substitutents are hydrogens, and propyl and methyl groups, and in the case of the quaternary ammonium salts the substituents are methyl and phenyl groups for **6**, and ethyl and methyl groups for **7**. It is known that the alkyl groups have a tendency to transfer.electron density to electron poor centers, resulting in the positive charge becoming more distributed on the molecule, and the cation becoming more stable. In the case of alkylammonium salts, the positive charge at nitrogen increases the acidity of the hydrogen atoms on the alkyl group, which leads to the Hoffman elimination. A similar increase in the acidity of the methyl group can result in its deprotonation by the monomethyl ester of the phosphonic acid to give a small equilibrium concentration of the alkylammonium salt **8** (Equation (9)). The most



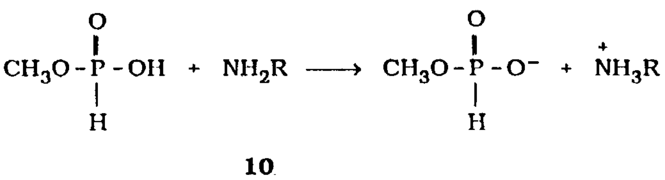
$$CH_3O-\underset{H}{\overset{\overset{O}{\|}}{P}}-O^- + \underset{CH_3}{\overset{+}{N}H_2R} \longrightarrow CH_3O-\underset{H}{\overset{\overset{O}{\|}}{P}}-OH + \underset{\underset{\mathbf{8}}{CH_2^-}}{\overset{+}{N}H_2R} \qquad (9)$$

likely pathway for the formation of **3** and **4** involves decomposition of the unstable salts **8** to a carbene **9** and an amine **10**, in a reaction that corresponds to the Hoffman elimination (Equation (10)). The amine **10** can then react with the monomethyl ester of



$$\underset{\underset{\mathbf{8}}{CH_2^-}}{\overset{+}{N}H_2R} \longrightarrow \underset{\mathbf{9}}{:CH_2} + \underset{\mathbf{10}}{NH_2R} \qquad (10)$$

phosphonic acid to give the ammonium salt (Equation (11)). The carbene can then subsequently undergo polymerization or oligomerization.



$$CH_3O-\underset{H}{\overset{\overset{O}{\|}}{P}}-OH + \underset{\mathbf{10}}{NH_2R} \longrightarrow CH_3O-\underset{H}{\overset{\overset{O}{\|}}{P}}-O^- + \overset{+}{N}H_3R \qquad (11)$$

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